DEPARTMENT OF THE ARMY
U.S. ARMY RESEARCH, DEVELOPMENT & ENGINEER COMMAND
EDGEWOOD CHEMICAL AND BIOLOGICAL CENTER
ABERDEEN PROVING GROUND, MARYLAND 21010-5424

REPLY TO ATTENTION OF:

AMSRD-ECB-CB-C 27 Apr 04

MEMORANDUM FOR Commander, U.S. Army Chemical Materials Agency, Project Manager, Non-Stockpile Chemical Material, ATTN: AMSCM-ECN-SO (Mr. Hoffman), Aberdeen Proving Ground, Maryland 21010-5424

SUBJECT: Method Detection Limit/Practical Quantitation Limit Study for GB and HD in Monoethanolamine to support the EDS

1. The ECBC Environmental Monitoring Laboratory (EML) conducted a Method Detection Limit (MDL)/ Practical Quantitation Limit (PQL) Study for GB in 45% monoethanolamine (MEA) and HD in 90% MEA. The lab followed the guidance in 40 CFR 136 Appendix B. Under this protocol, the MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

2. MEA Matrix: MEA is a neutralization reagent. In an agent destruction process, MEA would be added well in excess of the amount of agent. Only if one were to reach the point where all excess MEA were consumed/tied up as the salt, would breakthrough occur and agent residual be detectable in a sample.

According to 40 CFR 136, the test matrix should be free of interferences. The challenge for the MDL/PQL study was that an MEA/water sample prepared in the laboratory has not been reacted with agent and retains its full neutralization capability. The known amount of analyte spiked into an MEA/water sample in the laboratory will be partially or fully destroyed.

3. HD and Breakdown Products: According to Stuff, et. al.[1] the destruction of HD by MEA at room temperature is slow relative to the destruction of GB. They tested 73 wt% MEA/water and found that neutralization was sufficiently slow to permit its use as a test matrix. EML used 90% MEA/water to mimic the HD neutralization solutions being used in this project. The spike amount was adjusted to account for the 60% HD destruction seen during previous MEA analysis efforts. The expected 40% residual HD was observed.

The calculated MDLs and PQLs are shown in Table 1. Each of these values is lower than the stated requirement for sample monitoring. To reduce operator error in the field, a Reporting Limit of 0.25 mg/L is recommended, corresponding to the highest PQL calculated.

4. GB: Again from Stuff, et. al.[1], "spike and recovery studies for GB at the 1 μg/g level and lower using reaction masses were unsuccessful due to the reactive nature of the matrix. A surrogate matrix was used to simulate the reaction masses." After evaluation of the neutralization reaction, Stuff, et. al. used and recommend a 60 wt% solution of ethanolamine hydrochloride in water as a surrogate matrix to test the analytical method. Since the surrogate matrix simulates a fully spent neutralization agent, the GB is not destroyed.

EML used the recommended surrogate matrix for the GB MDL/PQL study. The matrix was spiked to achieve the desired reporting limit of not more than 1 mg/L. The surrogate matrix was extracted with methylene chloride, which achieves better extraction of GB than does hexane. To assure the appropriateness of this solvent, a 45% MEA/distilled water aliquot was mixed with an equal amount of methylene chloride. Solvent separation was good.

The calculated MDL and PQL are shown in Table 2. The calculated PQL of 0.11 mg/L is well below the stated requirement of 1.00 mg/L.

5. Field QC and Data Reporting: During field operations, each batch of samples will be controlled in accordance with the EML Internal Operating Procedure (IOP). Each batch will contain the QC samples shown in Table 3. The clean matrix for each batch will be the same as the matrix used during the MDL studies, i.e., 90% MEA for HD/BDP and 60% ethanolamine hydrochloride for GB.

After meeting calibration requirements as specified in the IOP, the LCS/LCSD will be used to assure that the total method is in control. Control limits are specified in Table 4. Spikes of field samples (matrix spikes) may be used to assist in identifying matrix effects on the analytical process, but will not be used to determine if the process is in control.

Samples with no detectable target analytes will be reported as less than (<) the PQL. Sample results between the MDL and PQL will be reported with a J flag.

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THOMAS E. ROSSO
Acting Chief, Program Management Team

[1] John R. Stuff, Richard L. Cheicante, Kevin M. Morrissey, H. Dupont Durst. "Trace Determination of Isopropyl Methylphosphonofluoridate (GB) and Bis (2-Chloroethyl) Sulfide (HD) in Chemical Neutralization Solutions by Gas Chromatography-Mass Spectrometry," *J. Microcolumn Separations*, 12(2) 87-92 (2000).

Table 1. One-Day HD and BDP MDL Study IAW 40 CFR 136 Appendix B

Target Analyte	Study Date	Spike Level (mg/L)	Effective Spike (mg/L)	MDL (mg/L)	Bias (Accuracy)	Precision	Practical Quantitation Limits (mg/L)	Comments
Mustard	4/20/2004	1.088	0.428	0.084	39.3%	6.8%	0.25	MEA destruction of HD reduces effective spike concentration.
1,4-Thioxane	4/20/2004	1.009	0.402	0.052	39.8%	4.5%	0.25 (0.16)	MEA destruction of HD reduces effective spike concentration.
1,4-Dithiane	4/20/2004	1.000	0.440	0.055	44.0%	4.3%	0.25 (0.17)	MEA destruction of HD reduces effective spike concentration.

Table 2. One-Day GB MDL Study IAW 40 CFR 136 Appendix B

Target Analyte	Study Date	Spike Level (mg/L)	MDL (mg/L)	Bias (Accuracy)	Precision	Practical Quantitation Limits (mg/L)	Comments
GB	4/20/2004	0.500	0.036	108.9%	2.3%	0.11	

Table 3. Quality Control Requirements
Agents and Related Breakdown Products

QC Sample	Frequency	Acceptance Limits	Corrective Action
Method Blank: Same matrix as used for MDL study	1 per batch of 20 or fewer samples	Target analytes less than reporting limit.	Reanalyze all samples associated with unacceptable blank.
Laboratory Control Spike (LCS) (using same matrix as for Method Blank) – spike target analytes	1 per batch of 20 or fewer samples	Recovery within control limits.	Reanalyze sample. If second analysis fails, re-extract and reanalyze all associated field samples with new QC samples.
Laboratory Control Spike Duplicate (LCSD) (using same matrix as for Method Blank) – spike target analytes	1 per batch of 20 or fewer samples	Recovery within control limits. Relative percent difference between LCS and LCSD within control limits.	If recovery outside limits, corrective action same as LCS. If RPD is greater than acceptance limit, reanalyze sample and duplicate; if still outside control limit, flag associated data.
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (using field sample)	1 each per batch of 20 or fewer samples	Same as LCS and LCSD	Discuss effect of matrix in report narrative

Table 4. Quality Control Acceptance Limits for LCS/LCSD Samples
Agents and Related Breakdown Products in MEA

Target Analyte	Mean % Recovery	% Recovery UCL and LCL	RPD UCL and LCL
HD in 90% MEA[1]	48.5%	15 – 82%	0 – 20%
1,4-Thioxane in 90% MEA[1]	61%	21 – 101%	0 – 23%
1,4-Dithiane in 90% MEA[1]	61%	34 – 90%	0 – 24%
GB in 60% ethanolamine hydrochloride[2]	100%	70 – 130%	0 – 25%

[1] Limits based on statistical analysis of more than 20 historical data points.

[2] Insufficient data points to perform statistical analysis. Limits are those generally applied until sufficient points collected.